



PATENT
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of)

10 LAURENT A. M. FENOUIL, BRENDAN D. MURRAY,)
and PAUL M. AYOUB)

Serial No. 10/789,115)

15 Filed February 27, 2004)

A PROCESS FOR PREPARING (BRANCHED-ALKYL))
ARYLSULFONATES AND A (BRANCHED-ALKYL))
ARYLSULFONATE COMPOSITION)20 COMMISSIONER FOR PATENTS
P. O. Box 1450
Alexandria, VA 22313-1450

25 Sir:

DECLARATION UNDER RULE 131

Brendan D. Murray hereby declares:

THAT he is a coinventor of the above-identified U.S. patent application; and

30 THAT he was awarded a B.A degree in Chemistry from The University of California
at Santa Cruz in 1980, and a Ph. D. degree in Chemistry from The University of California at Davis
in 1984; and

THAT he has worked in the field of this invention for 22 years for Shell; and

35 THAT he is familiar with US Patent 6,187,981 and that he understands that the
present application has been rejected as being anticipated by this patent and also as being obvious in
view of this patent because the patent was filed on July 19, 1999, which is before the priority date
of the present application; andTHAT the invention claimed in this application was made in the United States prior
to July 19, 1999; and

THAT the memorandum attached hereto from myself to H. L. Fong and T. B.

Thomason describes a proposal to make branched alkyl benzenes and their sulfonates by taking a linear paraffin mix produced by a Fischer-Tropsch process and hydrocracking and hydroisomerizing the linear paraffins to produce branched paraffins which would then be dehydrogenated to produce branched olefins which would then be used to make biodegradable branched alkyl benzenes, branched alkyl benzene sulfonates and derivatives thereof; and

5 THAT the experiment described on the third page of that memorandum shows that the present invention was reduced to practice prior to July 19, 1999, because a paraffinic wax which had been hydrocracked and hydroisomerized was fractionated to prepare a branched C₁₀₋₁₄ 10 paraffinic mixture which was then dehydrogenated at Westhollow Technology Center (WTC) in Houston, Texas using a platinum on alumina catalyst at a reaction temperature of 495°C, an operating pressure of 20 psig, and a molar hydrogen to hydrocarbon ratio of 4:1; and that a conversion of branched paraffins into branched C₁₀₋₁₄ olefins of 15 percent as measured by gas chromatography was achieved and that these branched olefins were separated from paraffins by 15 treatment with a 5A molecular sieve; and that this shows that the invention of claim 1, i.e., hydroisomerization and hydrocracking of a paraffin wax followed by dehydrogenation to produce branched olefins, was reduced to practice prior to July 19, 1999; and

15 THAT these branched olefins were reacted with benzene at a molar ratio of olefins: benzene of 1:20 at a reaction temperature of 190°C using acidic mordenite as the catalyst to alkylate the benzene and produce a branched alkyl benzene.

20 Brendan D. Murray further declares that all statements herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United 25 States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

30

Date July 23, 2007


Brendan D. Murray

Shell Chemical Company

A Division of Shell Oil Company



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From: B. D. Murray; Shell Chemical Co. CT-REC
To: H. L. Fong and T. B. Thomason
Subject: Unconventional Routes to Very Low Sulfur BAB/BABS

Introduction

Linear Alkyl Benzenes and their sulfonates are widely used in the production of many low cost detergents.¹ Detergent products based on LAB/LABS often compete directly with detergents based on Shell detergent range alcohols.² Shell has expressed an interest in participating in the LAB market as a means of growing the size of their Detergents business. In addition, Shell has also expressed an interest in using unconventional feedstocks such as products obtained from Shell's SMDS process to make LAB/LABS and Branched olefins, Branched Alkyl Benzenes (BAB), Branched Alkyl Benzene Sulphonates (BABS) and other BAB derivatives. These branched products should exhibit improved performance in detergent operations due to their physical properties. This proposal describes a method of producing branched olefins, BAB and BAB derivatives from highly hydrotreated kerosene and syngas (via F-T processes like SMDS).

Most LAB/LABS is prepared using routes that involve C₁₀-C₁₄ n-paraffins. The C₁₀-C₁₄ n-paraffins typically have physical properties like those listed in Table I.

Table 1. Desired Physical Properties of C₁₀-C₁₄ n-Paraffin Product for LAB

Carbon Distribution (% Wt.)	
C9-	<0.5
C10	12-18
C11	32-38
C12	28-34
C13	12-18
C14	1-7
C15	<0.2

Nitrogen (ppm)	<1
Sulfur (ppm)	<1
Halides (ppm)	<2
Aromatics (% Wt.)	<0.2
Olefins (% Wt.)	<1
n-Paraffins (% Wt.)	>99

CONDEA Vista and EXXON are currently the two main producers of C₉-C₁₇ n-paraffins in the USA.³ A larger supply of C₉-C₁₇ n-paraffins is produced outside of the USA. Shell has sold C₁₀-C₁₄ n-paraffins produced at the SMDS plant in Bintulu. The Bintulu C₁₀-C₁₄ n-paraffins made via the SMDS process have very low sulfur contents (<1 ppm) and thus do not require hydrotreating. During the F-T step in the SMDS process, a paraffinic wax with carbon numbers of up to around C₁₀₀ is produced. The paraffinic wax is converted to a mixture of lower carbon number paraffins by hydrocracking/isomerizing the wax. By controlling the conditions used in the hydrocracking/isomerizing the wax and the catalyst used, lower carbon number paraffins with varying degrees of branching can be obtained. These branched paraffins can be dehydrogenated to yield branched olefins. The branched olefins can be used to alkylate aromatics such as benzene branched to produce essentially sulfur free BAB which can be further converted into BABS and other valuable derivatives.

Technical Considerations

Recently, a study conducted for HODER demonstrated that marketable C₁₀-C₁₄ n-paraffins could be prepared at DPMC from a HVI 100 kerosene stream produced in the DU-1 column.⁴ The HVI 100 kerosene from DU-1 contains roughly 600 ppm S and thus requires extensive hydrotreating to reduce the sulfur level to 4 ppm or less. Microreactor testing conducted at WTC proved that the HVI 100 kerosene could be hydrotreated to <1.5 ppm using the current operating conditions of the DPMC HDU-1 hydrotreater. A further reduction in the sulfur concentration to < 1 ppm S is obtained by passing the hydrotreated HVI 100 kerosene through a normal paraffins recovery unit, (NPRU) such as the idled unit at DPMC. Recovery of the branched paraffins rejected by the NPRU would serve as a good source of low sulfur branched paraffins although obtaining essentially sulfur free branched paraffins from SMDS wax cracking is an even better source of branched paraffins. Branched paraffins obtained from wax cracking can be obtained with a wide range of carbon numbers and fractionated into narrower cuts such as C₇-C₃₅, C₇-C₁₈ or even C₁₀-C₁₄ paraffin fractions. A branched C₁₀-C₁₄ paraffin composition similar to that presented in Table 1 (except with significant reduced n-paraffin content) should be useful in making biodegradable BAB, BABS and derivatives.

Description of an Alternative Route to Branched C₁₀-C₁₄ BAB and BABS via SMDS wax cracking

The SMDS process produces a paraffinic wax that can be hydrocracked and hydroisomerized into a lighter isoparaffinic composition. Fractionation of the isoparaffinic product of wax cracking has been used to prepare narrower cuts. For example, a branched C₁₀-C₁₄ paraffinic mixture has been prepared after fractionation. This mixture richest in C₁₁-C₁₃ branched paraffins was dehydrogenated at WTC using a 0.5 wt. % Pt on alumina catalyst under the conditions recommended earlier by L. Fenouil.⁵ At a reaction temperature of 495°C, an operating pressure of 20 psig, and a molar hydrogen to hydrocarbon ratio of 4:1, a conversion of branched paraffins into branched C₁₀-C₁₄ olefins of 15% was measured by gas chromatography. These C₁₀-C₁₄ branched olefins were removed of paraffins by treatment with 5A molecular sieve.

BAB can be made by using the branched olefins diluted with paraffins or undiluted branched olefins to alkylate benzene. A simple experiment was performed using a 1:20 molar ratio of the C₁₀-C₁₄ branched olefins and benzene was performed to demonstrate this is a viable route to BAB. The alkylation was conducted at a reaction temperature of 190°C using acidic Mordenite as the catalyst. Other alkylation catalysts and reactions conditions can be used as mentioned in WO 99/05082 to prepare BAB and derivatives. This proposal seeks to further refine the conditions and optimize the catalysts used to make the branched olefins, BAB, BABS and derivatives.

I look forward to discussing this proposal further with you and I encourage you to add any suggestions that might improve the proposal. If you wish to pursue this proposal further, please discuss your funding options with Brent Shanks.

References

1. CEH Marketing Research Report: Normal Paraffins, No. 683.5000A, SRI International, 1998.
2. CEH Marketing Research Report: Linear Alpha-Olefins, No. 681.5030A, SRI International, 1997.
3. Chemical Marketing Reporter, 1998
4. B. D. Murray; TPR WTC 18-99, Microreactor Modeling Studies of the DPMC HDU-1: *HDS Performance Tests in Support of a Possible DPMC NPRU Restart*
5. L. Fenouil. E-mail note to P.Himelfarb and B. Murray dated January 29, 1998.